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ORIGINAL ARTICLE

# Ethyl benzene detection by BN nanotube: DFT studies

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**Abstract** Electrical sensitivity of a boron nitride nanotube (BNNT) was examined toward ethyl benzene ($C_8H_{10}$) molecule by using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level, and it was found that the adsorption energy ($E_{ad}$) of ethyl benzene on the pristine nanotubes is about −11.42 kJ/mol. But when nanotubes have been doped with Si, O, S. P atoms, the adsorption energy ($E_{ad}$) and recovery time changed and the sensitivity of the nanotubes as adsorbent of $C_8H_{10}$ molecule was increased. Calculations showed that when the nanotube is doping, the adsorption energy will be equal to −1.75 kJ/mol which leads to a decrease in the recovery time and also, due to doping the nanotube with O, the amount of HOMO/LUMO energy gap ($E_g$) will reduce significantly. It seems that nanotube (BNNT) is a suitable semiconductor after doping, and the doped BNNT in the presence of ethyl benzene an electrical signal is generating directly and therefore can potentially be used for ethyl benzene sensors, but BNNT is not a suitable adsorbent for $C_8H_{10}$ molecules.



## 1. Introduction

Ethyl benzene is a hazardous substance and is considered one of the environmental pollutants. Ethyl benzene adsorption for workers who are exposed to lead through inhalation and absorption through the skin is less [1,2]. In prolonged contact with the ethyl benzene causes fatigue, headache, eyes and nervous system is stimulated [3]. Low concentration of organic contaminants is approximately 100 ppm [4,5].

Since the discovery of carbon nanotube (CNT) by Iijima [6] the properties and applications of this novel material have been investigated extensively [7–9]. CNTs have recently emerged as a promising substitute for materials of different properties and various applications in hydrogen storage, gas sensors, textiles and many more [10,11]. Boron nitride nanotube (BNNT) has unique properties of a semiconductor behavior. The reason for such behavior is the total atomic number of B and N [12–14]. An interesting case for studying these BNNTs is investigating their composite type [15–17]. BNNT has a smaller band gap of a material that is interesting for

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applications in nanoscale devices [18]. BNNT has been composed of a single layer rotation of $sp^2$. BNNT's unique properties including tensile strength, stiffness and deformation are the features of this nanotube [19,24,25]. Previously adsorption of different molecules toward nanostructures has been studied [20–23]. In this study, the adsorption of ethyl benzene on the pristine case BNNT while Si, O, S, P atoms are in its structure has been investigated.

## 2. Computational methods

### *2.1. Computation procedures are include the following*

We have optimized the ethyl benzene molecule and BNNT at the B3LYP/6-31G(d) level of theory. BNNT is made up of 30N, 30B atoms were saturated by 10 hydrogen atoms which are in initial and end part of nanotube. The reason for this act had been done to decrease the boundary effects and totally nanotube is involving 70 atoms (Fig. 1).

The BNNT that has been selected is zigzag (5,0) type and GAMESS software [29] is used to perform these calculations. The B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [26–28].We made ethyl benzene molecule from different positions of the site to be close to the nanotube and its adsorption has been calculated by using the Eq. (1).

$$E_{ad} = E_{\text{Nanotube+Ethylbenzene}} - [E_{\text{Ethyl benzene}} + E_{\text{Nanotube}}] + \delta_{\text{BSSE}} \quad (1)$$

According to the mentioned equation $E_{\text{Ethyl benzene}}$ is ethyl benzene molecule's energy, $E_{\text{Nanotube}}$ is the nanotube energy and $E_{\text{Nanotube + Ethyl benzene}}$ is the nanotube's energy with ethyl benzene. In addition, $\delta_{\text{BSSE}}$ is representing the basis set super position error. In the following steps Si, O, S, P atoms in the nanotube structure have been doped to examine the ethyl benzene adsorption on the nanotube and conductivity which is doping with Si, P, S and O atoms.

## 3. Results and discussion

Fig. 1 shows the structure of boron nitride nanotube (BNNT), in order to obtain the most stable adsorption mode of $C_8H_{10}$ molecule on different positions of BNNT, the most stable configuration is shown in Fig. 2, that hydrogen atom in the ring at a distance of ethyl benzene is 3.16 A° far from boron atom of the nanotube and 2.93 A° far from nitrogen atom of the nanotube.

Detailed information of the structure and electronic properties of the BNNT including the HOMO/LUMO energy gap ($E_g$) are shown in Table 1 in which adsorption energy ($E_{ad}$) for mentioned configuration of ethyl benzene and nanotube is about −11.42 kJ/mol and then we calculated the HOMO/LUMO energy gap ($E_g$) for pristine nanotube since the ethyl benzene molecule is adsorbed on the nanotubes (Table 1). Diagram which shows HOMO/LUMO energy gap (*E*g) has been calculated, and the diagram which shows $E_g$ has been obtained by using density of state (DOS) software .

## 4. Adsorption of $C_8H_{10}$ on P and S doped BNNT

To examine the sensitivity of the adsorption of BNNT of $C_8H_{10}$ as an adsorbent for $C_8H_{10}$ its examining has been done two times, once B atom doped by P atom and other time N atom by P atom has been doped. Doped calculation of P on BNNT shows that the value of $E_g$ is less than the pristine nanotube (Fig. 3) and the best adsorption energy ($E_{ad}$) is obtained when Pchk the usage sitting instead of N and ethyl benzene has been adsorbed. DOS diagram clearly shows that when P is doped on the BNNT it will become a semiconductor.

Optimization of these type of interactions is desirable for gas detection but is not optimal because weak interactions such as these means that the BNNT is not suitable adsorbent for ethyl benzene molecule (Table 1). At this stage to examine the sensitivity of the adsorption of BNNT of $C_8H_{10}$ as an adsorbent for $C_8H_{10}$ once B atom by a S atom and other N atom by a S atom is doped. Doped calculation shows that

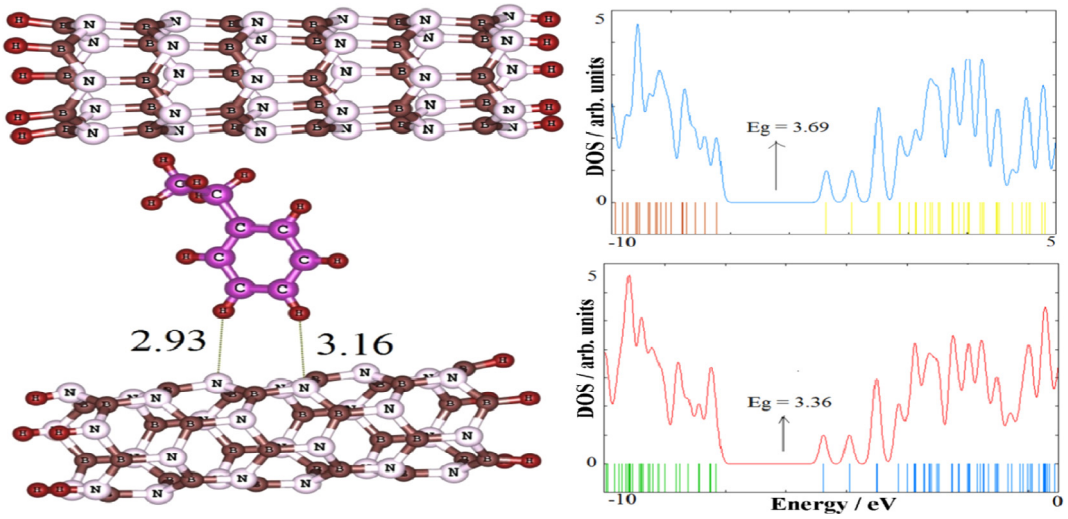


**Figure 1** Ethyl benzene adsorption on the BNNT and DOS diagram for observing $E_g$ of nanotube.

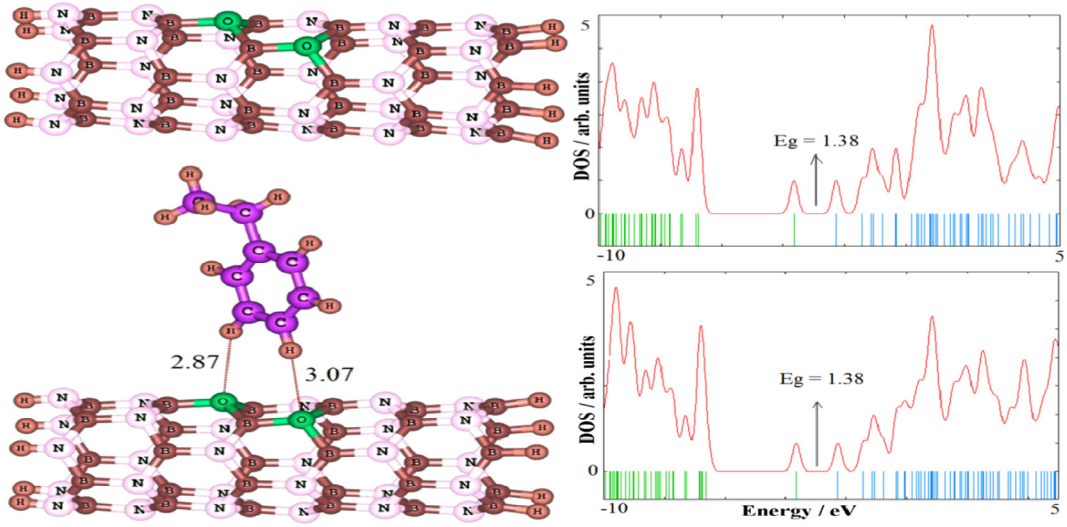


**Figure 2** Doped nanotube by O and DOS diagram for observing $E_g$ nanotube.

**Table 1** $E_{ad}$ (kJ/mol), eV for the others.

| System | $E_{ad}$ | $E_{HOMO}$ | $E_{FL}$ | $E_{LUMO}$ | $E_g$ | $^*\Delta E_g$ (%) |
|---|---|---|---|---|---|---|
| BNNT | – | −6.45 | −4.60 | −2.76 | 3.69 | – |
| E-BNNT | −11.42 | −6.06 | −4.38 | −2.70 | 3.36 | −8.9 |
| O | – | −3.66 | −2.97 | −2.28 | 1.38 | – |
| E-O | −1.75 | −3.65 | −2.96 | −2.27 | 1.38 | 0.0 |
| P | – | −6.42 | −4.61 | −2.81 | 3.61 | – |
| E-P | −6.01 | −6.13 | −4.47 | −2.82 | 3.31 | −8.3 |
| S | – | −3.73 | −3.08 | −2.44 | 1.29 | – |
| E-S | −4.36 | −3.74 | −3.08 | −2.43 | 1.30 | +0.7 |
| Si | – | −5.23 | −4.00 | −2.77 | 2.45 | – |
| E-Si | −5.98 | −5.13 | −3.93 | −2.73 | 2.40 | −2.0 |

the amount of the $E_g$ of S on the pristine nanotube is reduced (Fig. 4).

DOS diagram clearly shows that when S doped on the BNNT is a semiconductor, the doped BNNT is not suitable adsorbent for ethyl benzene molecule (Table 1). If $E_g$ is significantly increased then it is expected that recovery time will be long, meanwhile according to transition state theory and recovery time can be explain as Eq. (2)

$$\tau = \upsilon_0^{-1}\exp(-E_{ad}/kT) \tag{2}$$

where $T$ is the temperature, $k$ is the Boltzmann's constant, and $\upsilon_0$ is the attempt frequency.

According to this equation as often as adsorption energy ($E_{ad}$) is increasing the recovery time becomes longer and calculation in Table 1 shows that the recovery time and adsorption energy is not suitable level.

## 5. Adsorption of $C_8H_{10}$ on O and Si doped BNNT

At this stage doping has been studied with another element. First, instead of B atom in the boron nitride nanotube an O atom and then instead of N atom another O atom is replaced in a nanotube (Fig. 2), and then geometrical structures and

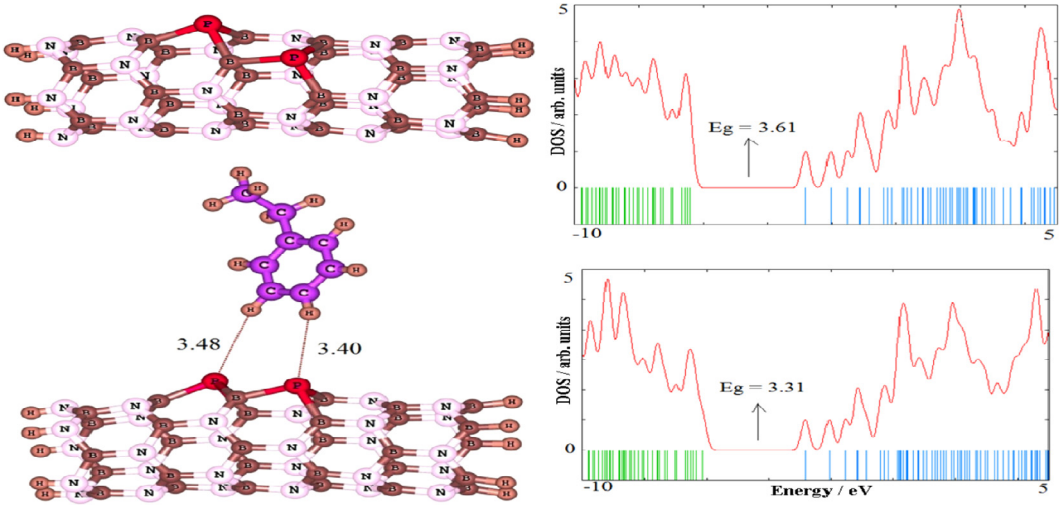


**Figure 3** Doped nanotube by P and DOS diagram for observing $E_g$ nanotube.

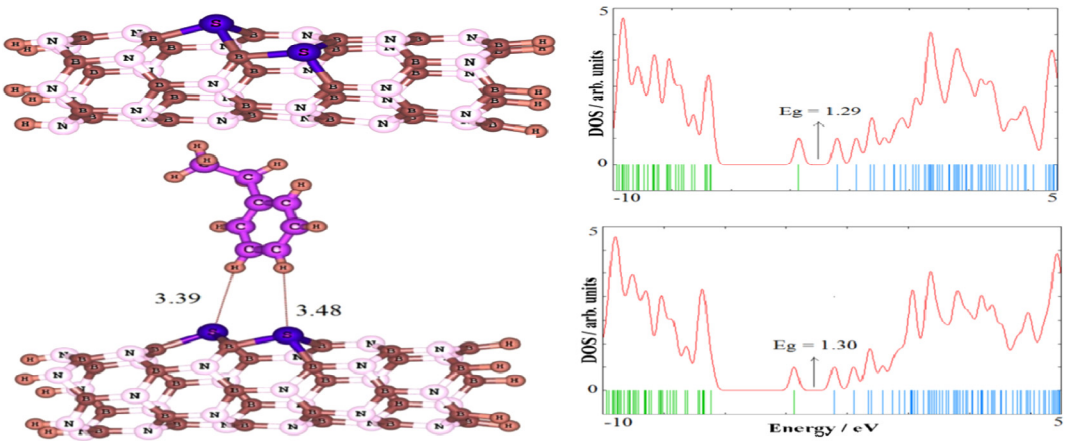


**Figure 4** Doped nanotube by S and DOS diagram for observing $E_g$ nanotube.

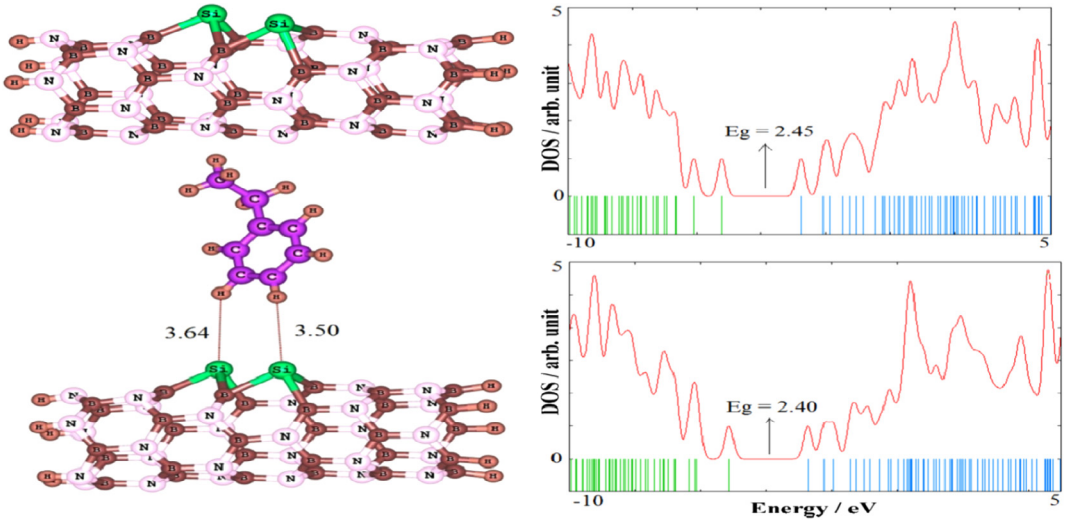


**Figure 5** Doped nanotube by Si and DOS diagram for observing $E_g$ nanotube.

electronic properties of BNNT are doped and their adsorption behavior are studied. Computations showed that when O is replaced by N in BNNT the $E_g$ will become less. At this stage to examine the sensitivity of the adsorption of BNNT of $C_8H_{10}$ as an adsorbent for $C_8H_{10}$ once B atom by a Si atom and other N atom by a Si atom is doped (Fig. 5), and then geometrical structures and electronic properties of BNNT are doped and their adsorption behavior are studied.

Computations showed that when Si is replaced by N in BNNT the $E_g$ will become more (Fig. 5) when O is sitting instead of N and B, and the adsorption energy of ethyl benzene on nanotube is less than when we just use the pristine nanotube (not doped). After adsorption of $C_8H_{10}$ on the mentioned nanotube that has been doped by O the HOMO/LUMO energy gap ($E_g$) will decrease and therefore a substantial increase will occur in conductivity and this phenomenon can be explained by Eq. (3), [26]

$$\sigma = \exp(-E_g/2kT) \tag{3}$$

where $\sigma$ is conductance, $T$ is temperature, $k$ is Boltzmann constant. According to this equation as often as $Eg$ is smaller it leads the conductivity to be more it can be concluded that when O is doping on BNNT, we think that the BNNT can be used as semiconductor, and by doping atoms in BNNT structure in the presence of ethyl benzene an electrical signal is generating directly and therefore can potentially be used for ethyl benzene sensors, but the results show BNNT is not a suitable adsorbent for ethyl benzene

## 6. Conclusion

The adsorption of ethyl benzene ($C_8H_{10}$) molecules on the surface of BNNT (boron nitride nanotube) has been studied by using density functional theory (DFT) and then we doped the Si, P, S and O atoms in the structure of the nanotube, the results show it is clearly possible to modif nanotubes as a semiconductor and the doped BNNT in the presence of ethyl benzene, an electrical signal is generated directly and therefore can potentially be used for ethyl benzene sensors, but the results show BNNT is not a suitable adsorbent for ethyl benzene. These results may open a new gate to chemically modifying the nanotubes in a way to expand the fields of their applications in industry and technology.

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